

Transport Phenomena in Fluids: Finite-size scaling for critical behavior

Sutapa Roy and Subir K. Das*

Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O, Bangalore 560064, India
(Dated: November 10, 2010)

Results for transport properties, in conjunction with phase behavior and thermodynamics, are presented at the criticality of a binary Lennard-Jones fluid from Monte Carlo and molecular dynamics simulations. Evidence for much stronger finite-size effects in dynamics compared to statics has been demonstrated. Results for bulk viscosity are the first in the literature that quantifies critical divergence via appropriate finite-size scaling analysis. Our results are in accordance with the predictions of mode-coupling and dynamic renormalization group theoretical calculations.

PACS numbers: 64.60.Ht, 64.70.Ja

Understanding the properties of fluids is important from both basic research as well as technological point of view. Particularly, fluid behavior in the vicinity of critical point poses many interesting questions of fundamental importance [1–8]. Fluids with short-range interactions, exhibiting gas-liquid and liquid-liquid transitions, are expected to have the static critical exponents $\beta = 0.325$, $\gamma = 1.239$, $\nu = 0.63$, $\alpha = 0.11$, respectively, for order-parameter, susceptibility (χ), correlation length (ξ) and specific heat, thus belonging to the three-dimensional Ising universality class [7]. On the other hand, it is expected that model H [8] should define the dynamic universality class for both the transitions. In dynamics the quantities of interest are shear (η) and bulk (ζ) viscosities, thermal diffusivity and its analog, the mutual diffusivity (D_{AB}) in a binary fluid, the critical singularities for which are given by [2–4]

$$D_{AB} \sim \xi^{-x_D}, \quad \eta \sim \xi^{x_\eta}, \quad \zeta \sim \xi^{x_\zeta}; \quad \xi \sim \epsilon^{-\nu}, \quad (1)$$

$\epsilon (= |T - T_c|/T_c)$ being a measure of the temperature (T) deviation from the critical value (T_c). In Eq. (1), exponents obey the scaling relations [2]

$$x_D = 1 + x_\eta, \quad x_\zeta = z - \frac{\alpha}{\nu}; \quad x_\eta = 0.068, \quad z = 3.068, \quad (2)$$

where z characterizes the divergence of relaxation time τ , at T_c , with system size L as

$$\tau \sim \xi^z \sim L^z. \quad (3)$$

In addition to other static and dynamic properties, particular focus of this work is to understand the critical behavior of bulk viscosity that describes the response of a fluid to a compression or expansion. Even though the study of bulk viscosity is thought to be important for compressible fluids, the theoretical prediction, as our simulation results will also reveal, for similar critical enhancement for both gas-liquid (compressible) and liquid-liquid (incompressible) transitions is certainly interesting. While there are experiments [9] probing the

critical behavior of ζ , simulations are rare [10–13] despite this being very important in the description of the damping of longitudinal sound waves. Dyer et al. [13] in fact pointed out the difficulty of studying bulk viscosity and suggested the need of significant effort to understand dynamics of continuous model fluids. The only noteworthy study of bulk viscosity in the context of criticality, so far, is due to Meier et al. [11] for gas-liquid transition of a single component Lennard-Jones (LJ) fluid who, however, did not quantify the critical divergence. While their data suffered from large error close to T_c , their observation of strong enhancement of ζ far above T_c ($\simeq 4.5T_c$), as is also observed by us, due to extremely slowly decaying pressure fluctuations, is very interesting. In fact, to the best of our knowledge, ours is the first simulation study of bulk viscosity that quantifies its critical divergence. In addition to confirming the theoretical predictions for critical exponents [2–4], this work also provides direct evidence for stronger size effect in dynamics compared to statics.

Apart from understanding the universality, computer simulations have been instrumental in providing many other details as far as static properties are concerned. In contrast, simulations of critical dynamics are very rare [11, 14, 15] the primary reason for which being the critical slowing down, as embodied in Eq. (3), that brings in additional complexity for the computation of dynamics over statics where finite-size effects are the only difficulty. Also, for molecular dynamics (MD) simulations in micro canonical ensemble, which is needed for perfect preservation of hydrodynamics, it is extremely difficult to control the temperature to the desired value for a prolonged period of time due to truncation error. This may be a necessity at temperatures close to T_c because of the presence of long-time tails [2, 16], particularly for quantities showing strong enhancement. All these problems combined together is suggestive of avoiding brute force method of simulating larger systems close to the critical point. The finite-size scaling method employed here to understand the results will demonstrate

that if appropriate strategy is devised, all these hurdles could easily be overcome. Apart from critical phenomena, such methods could be useful in the study of other slow dynamics, e.g., glassy dynamics, where tools from critical phenomena are being recently adopted to understand growing dynamic length in supercooled liquids [17].

We use a binary fluid ($A+B$) model [14, 18] where, for $r_{ij}(|\vec{r}_i - \vec{r}_j|) < r_c$, particles at \vec{r}_i and \vec{r}_j interact via [18?]
 $u(r_{ij}) = U(r_{ij}) - U(r_c) - (r_{ij} - r_c)(dU/dr_{ij})_{r_{ij}=r_c}$, while $u(r_{ij} \geq r_c) = 0$, with $U(r_{ij}) = 4\varepsilon_{\alpha\beta}[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]$ ($\alpha, \beta \in A, B$) being the standard Lennard-Jones (LJ) potential. For the choice $\varepsilon_{AA} = \varepsilon_{BB} = 2\varepsilon_{AB} = \varepsilon$, we have a fully symmetric model that gives a demixing transition at [14] $T_c^* = k_B T_c / \varepsilon = 1.4230 \pm 0.0005$, for $r_c = 2.5\sigma$. Phase diagram of such a system can be obtained from a semi-grandcanonical Monte Carlo (SGMC) simulation [19], where in addition to standard displacement trials, one introduces identity switch ($A \rightarrow B \rightarrow A$) moves, thus allowing for fluctuations in concentration $x_\alpha (= N_\alpha / \sum_\beta N_\beta)$ of species α . The distribution $P(x_\alpha)$ of concentration fluctuation has double and single peak structures respectively at temperatures below and above T_c . While from the location of the peaks below T_c one can obtain the phase diagram in $x_A - T$ plane, static concentration susceptibility (χ) above T_c can be calculated as $k_B T \chi = \chi^* T^* = N(\langle x_\alpha^2 \rangle - 1/4)$, where the term $1/4$ corresponds to a critical concentration $x_A^c = 1/2$ dictated by the symmetry of the model.

Transport properties were studied via MD simulations in microcanonical ensemble with ζ and the Onsager coefficient $\mathcal{L} (= \chi D_{AB})$ being calculated from Green-Kubo (GK) relations [18, 20]

$$\zeta + \frac{4}{3}\eta = \left(\frac{t_0^3}{\sigma V T^* m^2} \right) \int_0^\infty dt \langle \sigma'_{xx}(0) \sigma'_{xx}(t) \rangle, \quad (4)$$

$$\mathcal{L} = \left(\frac{t_0}{N T^* \sigma^2} \right) \int_0^\infty dt \langle J_x^{AB}(0) J_x^{AB}(t) \rangle, \quad (5)$$

where $\sigma'_{xx} = \sigma_{xx} - P$, $\sigma_{xx} (= \sum_{i=1}^N [m_i v_{ix} v_{ix} + \frac{1}{2} \sum_j (x_i - x_j) F_{xj}])$ being the diagonal elements of the stress tensor with $P = \langle \sigma_{xx} \rangle$ (GK formula for η in Eq. (4) contains the off-diagonal elements of stress tensor) and $J_x^{AB}(t) (= x_B \sum_{i=1}^{N_A} \vec{v}_{i,A}(t) - x_A \sum_{i=1}^{N_B} \vec{v}_{i,B}(t))$ is the concentration current with $\vec{v}_{i,\alpha}(t)$ being the velocity of particle i of species α at time t . In Eqs. (4) and (5), V is the volume of simulation box, m is the mass of a particle and $t_0 [= (m\sigma^2/\varepsilon)^{1/2}]$ is the LJ time unit, which we set to unity. All results for dynamics are obtained from MD runs, with integration time step $\Delta t = 0.005$, in a periodic cubic box of length L , in units of σ , after averaging over 160 independent initial configurations.

In Fig. 1(a) we show the results for χ as a function of ϵ for $L^* = L/\sigma = 10$ and 18.6. The continuous line there has a power-law form with exponent γ being fixed to its Ising value 1.239. While this confirms the Ising-like behavior, the consistency of the data for $L^* = 18.6$ with the solid line over the whole region is suggestive that finite-size effects did not appear yet. In view of the fact that finite-size effects were pointed out to be stronger in dynamics and a very strong background contribution was found in the study of mutual diffusion [14], we revisit it in the following.

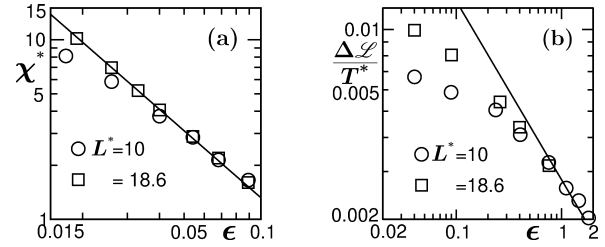


FIG. 1: (a) Log-log plot of χ vs. ϵ , for $L^* = 10$, and 18.6. The solid line represents the critical divergence of χ with exponent $\gamma = 1.239$. (b) Plot of Onsager coefficient $\Delta\mathcal{L}/T^*$ vs. ϵ for $L^* = 10$, and 18.6, on a log scale. This solid line here has critical exponent $\nu_\lambda = 0.567$ and amplitude $Q = 0.0028$.

In Fig. 1(b) we study the critical enhancement $\Delta\mathcal{L}(T) [= \mathcal{L} - \mathcal{L}_b]$ of Onsager coefficient, with \mathcal{L}_b being the contribution coming from short-range fluctuations and needs to be taken care of far above T_c , where critical enhancement is small. In the following we treat \mathcal{L}_b as a constant, albeit weak temperature dependence that it might have. Here we plot $\Delta\mathcal{L}(T)$ which has the expected critical divergence

$$\Delta\mathcal{L} = QT\epsilon^{-\nu_\lambda}; \quad \nu_\lambda = 0.567, \quad (6)$$

as a function of ϵ , by adopting the constant value of $\mathcal{L}_b = 0.0033$ as obtained in an earlier study [14]. Upon imposing [14] $Q = 0.0028$ and $\nu_\lambda = 0.567$, good consistency of the solid line is obtained with the simulation data, for large ϵ . This, in addition to directly confirming the theoretical predictions as well as the conclusion drawn from the previous finite-size scaling study [14], with very limited data, regarding the exponent and amplitude, is also indicative of a rather wide critical range. On the other hand, it is interesting to note from the comparison between Fig. 1(a) and Fig. 1(b) that size effects are appearing much earlier in \mathcal{L} than in χ , which requires appropriate attention to understand. With the knowledge about the spread of the critical region, we move forward to devise a strategy for a finite-size scaling analysis [6, 19, 21], that will require only small systems and large temperatures so that difficulty due to long-time tails could be avoided. This will be tested

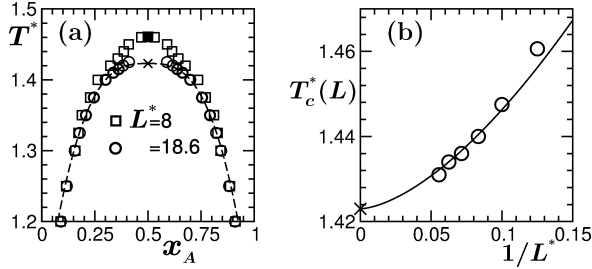


FIG. 2: (a) Phase diagram of the model in $x_A - T$ plane for two system sizes. The filled symbol corresponds to T_c^L for $L^* = 8$, while the cross (\times) locates $T_c^\infty \equiv T_c$. The dashed line there is a fit to the form $m = |x_A - 1/2| \sim \epsilon^\beta$, taking data close to the critical point and unaffected by finite size. (b) Plot of T_c^L vs. $1/L^*$ where the continuous line is a fit to the form (7) with $\nu = 0.63$, including only the four largest system sizes.

with the better understood quantities, χ and \mathcal{L} first, before applying it to ζ .

As a first step, in Fig. 2(a) we show the phase behavior of the present model for different values of L that exhibit strong size effect close to the critical point. We define a finite-size critical point [22], T_c^L , as the temperature where $P(x_A)$ in the SGM simulation gets a single-peak structure from a double-peak one with the increase of temperature. This is represented by filled symbol for $L^* = 8$. Note that true meaning of a critical temperature can be assigned only when $L \rightarrow \infty$, which for the present case is marked by a cross and was obtained [14] in an unbiased manner from the method of intersection of Binder parameter [23]. In Fig. 2(b) we demonstrate the variation of T_c^L with L . The continuous line there is a fit (including data only for four largest values of L^*) to the expected scaling form in the large L limit,

$$(T - T_c^L) \sim L^{-1/\nu}. \quad (7)$$

The deviation of data for $L^* = 10$ and 8 are due to corrections to scaling for small values of L , which can be numerically accounted for [5, 6] by replacing L^* by $L^* - \ell^*$ in the abscissa. Indeed for $\ell^* = 2$ we get a perfect fit passing through all data points, which, in fact, has been used to obtain T_c^L for intermediate L values. Nevertheless, even for $L^* = 8$, correction is very small and the simulation data deviates from the solid line by less than 1% which is negligible compared to the thermal fluctuations during the MD runs.

At this stage, we define an effective finite-size critical point [6] from $T_c^L [= T_c^L(1)]$ as

$$T_c^L(f) = T_c + f(T_c^L - T_c), \quad (8)$$

which has the same power-law convergence to T_c as (7). One can study critical behavior along different f -loci as

a function of L , when, for an observable $\mathcal{O} (\sim \epsilon^{x_{\mathcal{O}}})$, one obtains the scaling law

$$\mathcal{O} \sim L^{-x_{\mathcal{O}}/\nu}, \quad (9)$$

where the amplitude will depend upon the value of f . Fig. 3 demonstrates this for χ and $\Delta\mathcal{L}$ for two values of f , where we have plotted $\chi^{\nu/\gamma}$ and $(\frac{\Delta\mathcal{L}}{T})^{\nu/\nu_\lambda}$ vs L . A linear behavior upon imposing $\nu = 0.63$, $\gamma = 1.239$ and $\nu_\lambda = 0.567$ validates this strategy. Note that largest value of f considered here is 65 which gives $T_c^L(65) = 3.875$ for $L^* = 8$. Nice consistency of the data for whole range of L is suggestive of only weak corrections even for the smallest L considered.

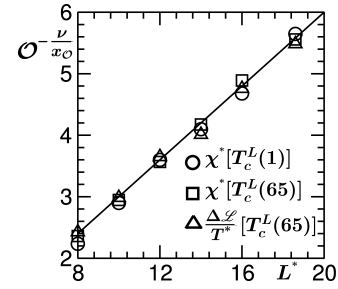


FIG. 3: Plots of $\chi^{*\nu/\gamma}$ and $(\frac{\Delta\mathcal{L}}{T})^{\nu/\nu_\lambda}$ vs. L^* along different f -loci. Data for different quantities and f values have been appropriately scaled to collapse. The continuous straight line is a guide to the eyes.

Having demonstrated the usefulness of such method, encapsulated in Eqs. (8) and (9), we adopt it to quantify the critical divergence of ζ . Due to the technical difficulties to calculate it at lower temperatures for larger systems, in Fig. 4(a) we present it only for $f = 65$. Very linear look of the whole data set on a log-log plot is suggestive of only small background contribution. Significant increase of ζ over only small range of $L^* \in [8, 12]$, signals a strong divergence. The continuous line there is a fit to a power-law form $\sim L^{x_\zeta}$ giving $x_\zeta \simeq 2.96$ which differs only by 2% from the theoretical prediction (almost indistinguishable dashed line) $z - \frac{\alpha}{\nu} \simeq 2.89$. Note that more recently [3] it has been pointed out that the exponent is closer to z . While this confirms the expected theoretical behavior, we estimate the non-universal critical amplitude from the following exercise which will also provide a more direct confirmation of the exponent. In Fig. 4(b), we plot ζ as a function of ϵ . Here, from our experience with \mathcal{L} , we choose a range with $\epsilon > 1$ (that includes the last four points) for a fitting to the form $\zeta \sim \epsilon^{-\nu x_\zeta}$ by fixing x_ζ to 2.89, which gives a critical amplitude $A_\zeta = 6.6 \pm 1.0$. Here the point of deviation of the simulation data from the solid line is consistent with the appearance of finite-size effect in \mathcal{L} . While the solid line provides an excellent fit to the selected region, an effective, though much

smaller and misleading, exponent could also have been obtained from a fitting to the whole data set which has an average linear look on log-scale.

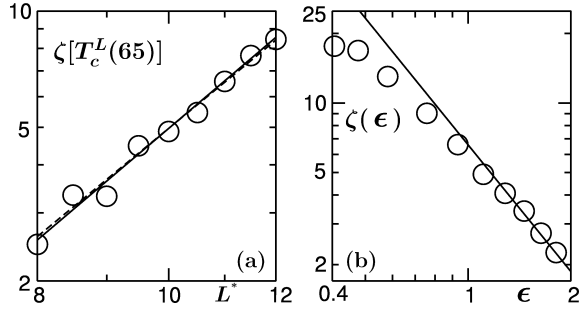


FIG. 4: (a) Log-log plot of ζ as a function of L at $T_c^L(f)$ with $f = 65$. The continuous line is a fit to $\sim L^{x_\zeta}$ giving $x_\zeta = 2.96$ while the dashed line corresponds to an exponent 2.89. (b) Plot of ζ vs ϵ for $L^* = 10$. The solid line is a fit to the form $A_\zeta \epsilon^{-1.82}$ giving $A_\zeta = 6.6 \pm 1.0$.

In summary, dynamic critical phenomena is studied in a symmetric binary fluid. Consistency with predictions of dynamic renormalization group and mode-coupling theories has been established. Quantitative understanding of the bulk viscosity via computer simulation is the first in the literature. Critical region appears to be rather wide so that with appropriate application of finite-size scaling method it has been possible to stick to only small systems at large temperatures. A possible reason for stronger finite-size effects in dynamics compared to statics could be back-flow due to periodic boundary conditions – however, significant attention is required to settle this important issue.

Acknowledgment: SKD acknowledges previous fruitful collaboration with M.E. Fisher, K. Binder, J.V. Sengers and J. Horbach. He also thanks K. Binder, J.V. Sengers and J.K. Bhattacharjee for critical reading of the manuscript and useful comments. The authors acknowledge grant number SR/S2/RJN-13/2009 of the Department of Science and Technology, India. SR is also grateful to CSIR, India, for financial support.

* das@jncasr.ac.in

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